SIAM J. APPL. MATH.
Vol. 45, No. 3, June 1985

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FLAMES WITH CHAIN-BRANCHING/CHAIN-BREAKING KINETICS*

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Abstract. A steady plane flame subject to the chain-branching/chain-breaking kinetics

$$A+X\rightarrow 2X,\qquad 2X+M\rightarrow 2P+M$$

is considered for a certain distinguished limit of parameter values corresponding to fast recombination. Here A is the reactant, X the radical, P the product, and M a third body. The activation energy of the production step is very large, while that of the recombination step is small and taken to be zero. These kinetics are the most attractive of the two-step schemes that have been proposed for explaining interesting phenomena not covered by one-step kinetics, and the purpose is to provide a firm foundation for exploitation of the scheme.

The object is to find the "laminar-flame eigenvalue" Δ, representing the burning rate, as a function of r, which is essentially the ratio of the two reaction rates. The response function $\Delta(r)$ is described by numerical integration and by asymptotic analysis for $r\rightarrow 0, \infty$.

1. Introduction.

Although the one-step irreversible reaction with large activation energy has served combustion theory well (see Buckmaster and Ludford [1]), the neglect of radicals excludes important phenomena. A particularly promising modification in this respect is the two-step irreversible reaction

$$A+X\rightarrow 2X,\qquad 2X+M\rightarrow 2P+M \tag{1}$$

consisting of a chain-branching (production) step and a chain-breaking (recombination) step. Here A is the reactant, X the radical, P the product, and M a third body. The activation energy of the production step is very large, while that of the recombination step is small and taken to be zero. The reaction was suggested by Zeldovich [2], who considered an isothermal production step; we shall generalize by allowing this step to be exothermic or even endothermic also. (Endothermic recombination is excluded on physical grounds.) The model was later discussed by Liñán [3] using activation-energy asymptotics.

So far the asymptotic model has been exploited by Seshadri and Peters [4]—see, however, Tam and Ludford [5], [6]—and by Ludford and Peters [7]. Of particular interest is fast recombination, when both the production and recombination of radicals take place in the same thin zone. All these authors assumed that the burning rate of a steady plane flame increased with the production rate in this (distinguished) limit; and, while this property can be argued on physical grounds, the present paper gives a mathematical derivation. In any event, the other properties of such a flame that are derived here provide a firm foundation for the subsequent exploitation of the model that will undoubtedly take place.

The plan of the paper is as follows. Sections 2 and 3 derive the basic limit equations and solve them numerically, not a trivial task. The properties of the solution for disparate production and recombination rates are then developed in §§ 4 and 5.

* Received by the editors July 17, 1984, and in revised form September 22, 1984. Computing time provided by the Cornell Materials Science Center, through Prof. W. H. Sachse, is gratefully acknowledged.

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2. Basic equations. For the reaction (1) the dimensionless equations of a steady plane flame are

$$\frac{dX}{dx}-\mathscr{K}^{-1}\frac{d^2X}{dx^2}=\mathscr{D}_1XYe^{-\theta/T}-\mathscr{D}_2X^2, \tag{2}$$

$$\frac{dY}{dx}-\mathscr{L}^{-1}\frac{d^2Y}{dx^2}=-\mathscr{D}_1XYe^{-\theta/T}, \tag{3}$$

$$\frac{dT}{dx}-\frac{d^2T}{dx^2}=\mathscr{D}_1q_1XYe^{-\theta/T}+\mathscr{D}_2q_2X^2. \tag{4}$$

Here X, Y, and T are the mass fractions of radical and reactant, and the temperature (respectively); $\mathscr{K}$ and $\mathscr{L}$ are the Lewis numbers of radical and reactant;

$$\mathscr{D}_1=D_1/M^2 \quad \text{and} \quad \mathscr{D}_2=D_2/M^2, \tag{5}$$

where D_1 and D_2 are the rate constants of the reaction steps; q_1 and q_2 are the proportions of the total heat released in the first and second steps of the reaction, so that

$$q_1+q_2=1; \tag{6}$$

and θ is the activation energy of the first step, that of the second step being taken as zero. Sometimes D_1 and D_2 are given a certain temperature dependence (Seshadri and Peters [4]), which merely results in a density-weighting of the coordinate x normal to the flame (von Mises transformation); when the flame is plane but unsteady, it results in considerable simplification (Ludford and Peters [7]), as is well known for single-step reactions. Given the parameters $\mathscr{K}$, $\mathscr{L}$, D_1, D_2, q_1/q_2, and θ, the problem is to determine the burning rate M for which these differential equations have a solution satisfying the boundary conditions

$$X,\ Y,\ T\to 0,\ Y_f,\ T_f \quad \text{as } x\to-\infty, \qquad X,\ \frac{dY}{dx},\ \frac{dT}{dx}\to 0 \quad \text{as } x\to+\infty. \tag{7}$$

The solution is sought in the limit $\theta\to\infty$ and, in general, involves numerical integration with jump conditions at the flame sheet ($x=0$) derived from the corresponding structure problem. Of special interest, however, is the fast-recombination case

$$\mathscr{D}_2=\theta^3D \tag{8}$$

when the chain-breaking step (1b), instead of being spread over the whole range of x, is confined to the flame sheet of the chain-branching step (1a). Then (effectively) $X=0$ and the simple formulas (11), (12) hold outside the flame sheet.

The absence of radicals outside a zone of thickness $O(\theta^{-1})$ at the origin is seen from (2) after dropping the $\mathscr{D}_1$-term and using the value (8). Setting

$$X=X_0(x)+\theta^{-1}X_1(x)+\theta^{-2}X_2(x)+\cdots \tag{9}$$

in the result gives, successively,

$$X_0=X_1=X_2=0. \tag{10}$$

The conclusion $X_0=0$ is actually reached for any $\mathscr{D}_2\to\infty$, but only for the distinguished limit (8) does the recombination zone have the same $O(\theta^{-1})$ thickness as the production zone (see below), so that the radicals play a significant role throughout the latter.

To determine Y and T we insert the analogues of the expansion (9) in equations (3) and (4) with right sides zero. Thus, the leading terms and their perturbations are found to be

$$x<0: \quad Y_0 = Y_f(1-e^{\mathscr{L}x}), \quad Y_1 = 0, \quad T_0 = T_f + Y_f e^x, \quad T_1 = 0, \tag{11}$$

$$x>0: \quad Y_0 = Y_1 = 0, \quad T_0 = T_f + Y_f, \quad T_1 = 0. \tag{12}$$

In the first instance $Y_1 = A\, e^{\mathscr{L}x}$ ahead of the flame sheet, but the integration constant A is zero when the origin of x is chosen appropriately. Likewise T_0 and T_1 are found to be constants behind the flame sheet, whose values must be fixed by the requirement

$$T \to T_f + Y_f \equiv T_b \quad \text{as } x \to +\infty; \tag{13}$$

continuity of T_0 and T_1 then yields the results (12c, d). (The general requirement (13) is obtained by integrating $q_2(2)+(3)+(4)$ from $-\infty$ to $+\infty$.)

The structure of the flame sheet, i.e. the production/recombination zone, is investigated by means of the expansions

$$\begin{gathered} X = \theta^{-1}\tilde{X}_1(\xi) + \theta^{-2}\tilde{X}_2(\xi) + \cdots, \qquad Y = \theta^{-1}\tilde{Y}_1(\xi) + \theta^{-2}\tilde{Y}_2(\xi) + \cdots, \\ T = T_b + \theta^{-1}\tilde{T}_1(\xi) + \theta^{-2}\tilde{T}_2(\xi) + \cdots, \end{gathered} \tag{14}$$

where

$$\xi = \theta x. \tag{15}$$

The expansion parameter θ^{-1} comes from the requirement that the temperature vary by no more than $O(\theta^{-1})$ in the zone, so that significant reaction takes place; then the stretching (15) ensures that temperature gradients are of the same order inside and outside the zone, as is needed for matching; and the leading terms in X and Y are zero because matching requires them to be so.

Setting the expansions in (2)-(4) yields the structure equations

$$\mathscr{K}^{-1}\frac{d^2\tilde{X}_1}{d\xi^2} - D\tilde{X}_1^2 = -\mathscr{L}^{-1}\frac{d^2\tilde{Y}_1}{d\xi^2} = q_1^{-1}\frac{d^2\tilde{T}_1}{d\xi^2} + Dq_1^{-1}q_2\tilde{X}_1^2 = -\tilde{\mathscr{D}}\tilde{X}_1\tilde{Y}_1\, e^{\tilde{T}_1/T_b^2} \tag{16}$$

where

$$\tilde{\mathscr{D}} = \mathscr{D}_1\theta^{-3}\, e^{-\theta/T_b}. \tag{17}$$

Note how the distinguished limit (8) ensures that the second reaction is comparable to the existing reaction and diffusion on the scale (15). To these equations must be added boundary conditions coming from matching with the expansions on either side of the flame sheet. Using the result (10)-(12), we find

$$\tilde{X}_1 = \begin{cases} o(1), \\ o(1), \end{cases} \quad \tilde{Y}_1 = \begin{cases} -\mathscr{L}Y_f\xi + o(1), \\ o(1), \end{cases} \quad \tilde{T}_1 = \begin{cases} Y_f\xi + o(1), \\ o(1), \end{cases} \quad \text{as } \xi \to \mp\infty. \tag{18}$$

The differential equations (16) imply that $q_2\mathscr{K}^{-1}\tilde{X}_1 + \mathscr{L}^{-1}\tilde{Y}_1 + \tilde{T}_1$ is a linear function of ξ, which the boundary conditions (18) show to be identically zero:

$$q_2\mathscr{K}^{-1}\tilde{X}_1 + \mathscr{L}^{-1}\tilde{Y}_1 + \tilde{T}_1 = 0. \tag{19}$$

The coefficient function $\tilde{X}_1$ can therefore be eliminated from the problem which, under the transformation

$$\tilde{T}_1 = -T_b^2 u, \quad \tilde{Y}_1 = \mathscr{L}T_b^2 v, \quad \xi = T_b^2\eta/Y_f, \tag{20}$$

then becomes

$$(21)\qquad q_2\frac{d^2u}{d\eta^2}=q_1 r\Delta(u-v)v\,e^{-u}+\Delta(u-v)^2,\qquad q_2\frac{d^2v}{d\eta^2}=r\Delta(u-v)v\,e^{-u},$$

$$(22)\qquad u,\,v=\begin{cases}-\eta+o(1),\\ o(1),\end{cases}\quad \text{as } \eta\to\mp\infty,$$

where

$$(23)\qquad \Delta=\mathcal{K}^2T_b^6D/Y_f^2,\qquad r=\mathcal{L}\tilde{\mathcal{D}}/\mathcal{K}D.$$

According to the definitions (5), (8), (17) the burning rate M appears in Δ via $D=\theta^{-3}\mathcal{D}_2=\theta^{-3}D_2/M^2$; but not in r, which depends only on the ratio $\mathcal{D}_1/\mathcal{D}_2=D_1/D_2$.

Determining M as a function of the parameters $\mathcal{K}$, $\mathcal{L}$, D_1, D_2, q_1/q_2, and θ is now seen to be equivalent to determining the function $\Delta(r)$ for which the problem (21)-(23) has a solution. The remainder of the paper is concerned with describing this latter function

$$(24)\qquad \Delta=F(r;q_1),$$

where the dependence on q_1 has been made explicit. We shall limit the discussion to

$$(25)\qquad -1<q_1\leqq 1,\quad \text{i.e.,}\quad 0\leqq q_2<2.$$

The restriction $q_2\geqq 0$ has a physical basis: bonding is never endothermic. While the need for the restriction $q_1>-1$ is not clear physically, it does not seem to be of significance. It arises analytically when r is large, i.e. when the production step is much faster than the recombination step.

3. Numerical integration. It is convenient to write the problem in the form

$$(26)\qquad \frac{du}{d\eta}=p,\qquad \frac{dp}{d\eta}=q_1r\Delta w(u-q_2w)\,e^{-u}+q_2\Delta w^2,$$

$$(27)\qquad \frac{dw}{d\eta}=q,\qquad \frac{dq}{d\eta}=-r\Delta w(u-q_2w)\,e^{-u}+\Delta w^2,$$

$$(28)\qquad u=\begin{cases}-\eta+o(1),\\ o(1),\end{cases}\quad p=\begin{cases}-1+o(1),\\ o(1),\end{cases}\quad w,\,q=o(1)\quad \text{as } \eta\to\mp\infty,$$

where, according to the result (19) and the definitions (20),

$$(29)\qquad w=(u-v)/q_2$$

is essentially the radical fraction. The problem (26)-(28) therefore governs $\tilde{T}_1$ and $\tilde{X}_1$.

The behavior of the system (26), (27) at its singular points $\eta=\pm\infty$ is complicated. Some remarks are made in the Appendix, and a theoretical study continues with a view to proving the existence of a value of Δ (depending on r and q_1) for which there is an orbit joining the singular points. (In the numerical work it was more convenient to assign Δ and determine r.)

This behavior was undoubtedly responsible for the failure of straightforward shooting from $\eta=-A$ to $\eta=B$ or vice versa (with $A, B>0$ and large). We therefore turned to the following minimization method. Define nine parameters

$$(30)\qquad r_1=r,$$

$$(31)\qquad r_2=u(-A),\quad r_3=p(-A),\quad r_4=w(-A),\quad r_5=q(-A),$$

$$r_6 = u(B), \quad r_7 = p(B), \quad r_8 = w(B), \quad r_9 = q(B); \tag{32}$$

then

$$\begin{aligned} J(r_1, r_2, \cdots, r_9) = {} & [u(0+) - u(0-)]^2 + [p(0+) - p(0-)]^2 + [w(0+) - w(0-)]^2 \\ & + [q(0+) - q(0-)]^2 + (r_3 + 1)^2 + r_5^2 + r_7^2 + r_9^2 \end{aligned} \tag{33}$$

is a function determined by integrating the system (26), (27) from $-A$ to 0 and (backwards) from B to 0. The value of r (for each Δ, q_1) can be found by minimizing J over the parameter $(=r_1)$ and the two sets of initial conditions (r_2, r_3, r_4, r_5), (r_6, r_7, r_8, r_9). Fast convergence was obtained whenever the starting estimates of r and these initial conditions were sufficiently accurate. The latter can be based on the asymptotic behavior of the solution as $\eta \to \pm\infty$.

The Appendix shows that, for a large value of A, we may expect

$$r_2 = A + 6q_2/\Delta A^2, \quad r_3 = -1 + 12q_2/\Delta A^3, \quad r_4 = 6/\Delta A^2, \quad r_5 = 12/\Delta A^3 \tag{34}$$

to be good estimates of the initial condition at $\eta = -A$; and that, for large B, we may expect

$$r_6 = 6q_2/\Delta B^2, \quad r_7 = -12q_2/\Delta B^3, \quad r_8 = 6/\Delta B^2, \quad r_9 = -12/\Delta B^3, \tag{35}$$

which are again independent of r, to be good estimates of the initial conditions at $\eta = B$ when r is greater than 1.

In determining the curve (24) for an assigned value of q_1, a guess for r and the estimates (34), (35) were only used to obtain the values of r for two close values of Δ. After that a continuation method was introduced to obtain estimates of Δ, r $(=r_1)$, $r_2, \cdots, r_9$ at a neighboring point on the curve. (During the subsequent minimization, Δ was held fixed.)

Figure 1 shows typical u- and w-profiles. (A and B were set equal to 10 in all the numerical work reported.) The smooth agreement at $\eta = 0$ of the left and right integrations is evident. Figure 2a gives the r, Δ-curves (24) for various values of q_1 less than 1, i.e. $q_2 > 0$. In particular, two negative values of q_1 are included, corresponding to endothermic production steps. Figure 2b shows the extreme curve $q_1 = 1$ and a curve with q_1 close to its limit -1.

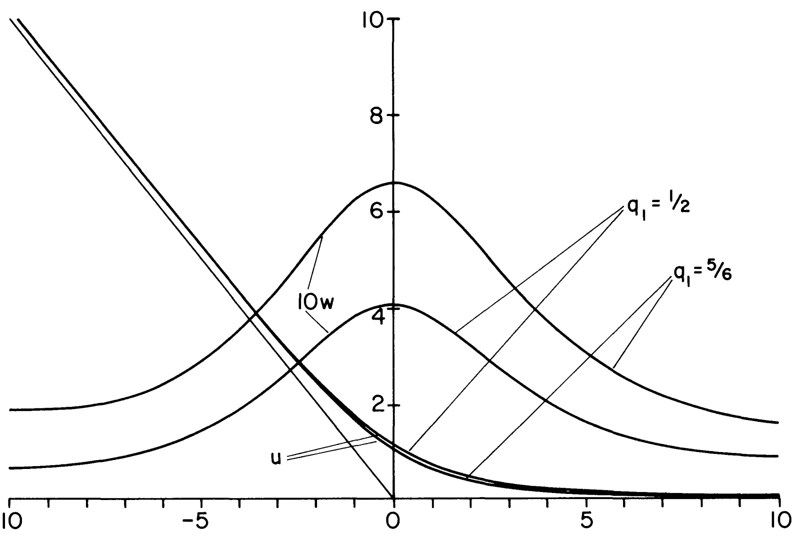

FIG. 1. *Profiles of u and w for* $\Delta = 2q_2$.

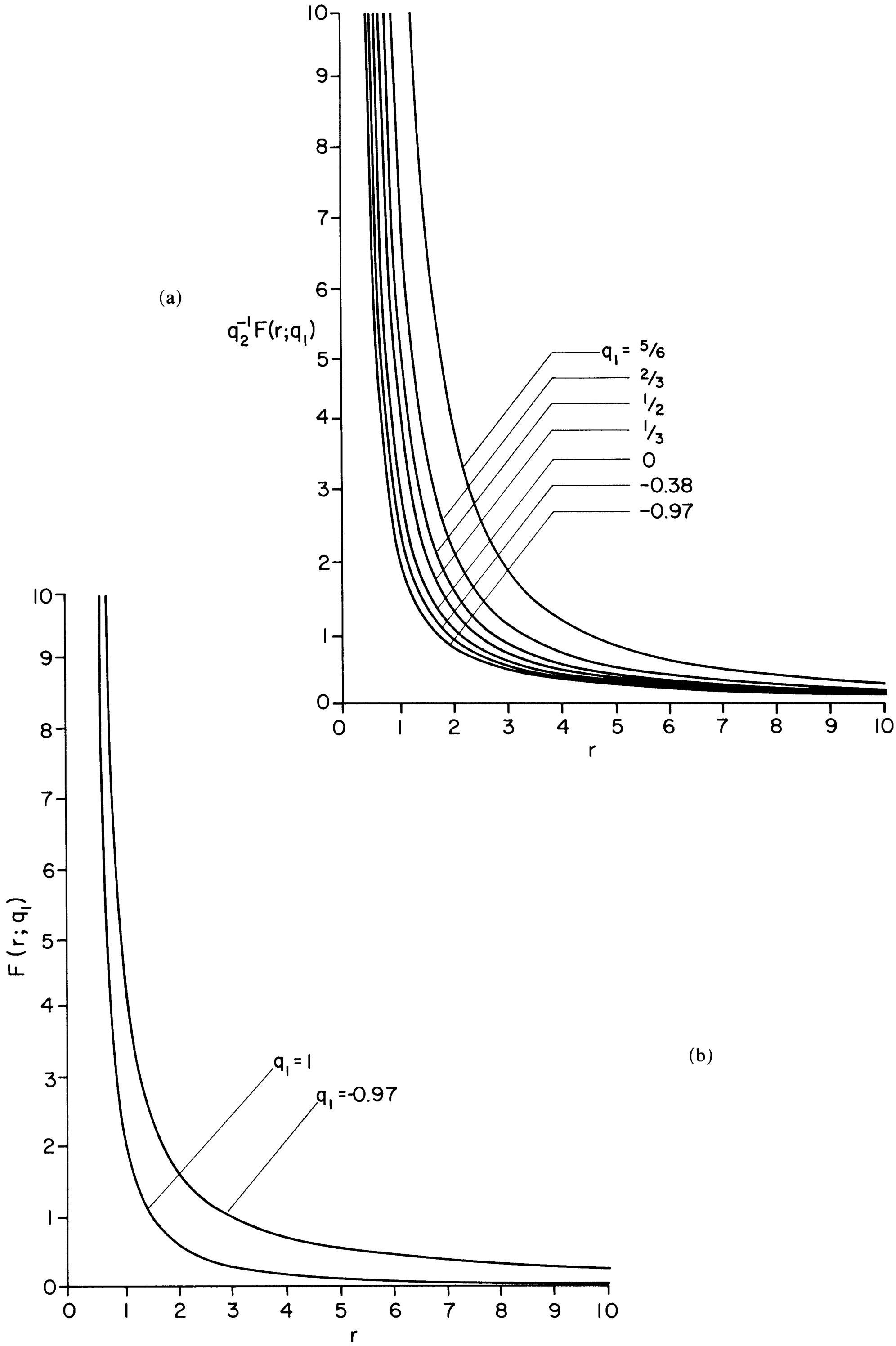

FIG. 2. *The response function* (24). *The chain-branching step is exothermic for* $q_1 > 0$, *isothermal for* $q_1 = 0$, *and endothermic for* $q_1 < 0$. *The chain-breaking step is never endothermic* ($q_1 \leqq 1$). (a) *Ordinate* Δ/q_2 *used to separate curves.* (b) *Band in which curves lie.*

4. Behavior as $r \to 0$. The numerical results indicate that $\Delta \to \infty$ as $r \to 0$ on each curve $q_1 = \text{const}$. To determine the asymptotic form of the curve, we use u as independent variable to write the problem (26)-(29) in the form

$$p\frac{dp}{du} = q_1 r\Delta w(u - q_2 w)\, e^{-u} + q_2 \Delta w^2, \quad p\frac{dw}{du} = q,$$
$$p\frac{dq}{du} = -r\Delta w(u - q_2 w)\, e^{-u} + \Delta w^2, \tag{36}$$

$$p = \begin{cases} -1 + o(1), \\ o(1), \end{cases} \qquad w,\, q = o(1) \quad \text{as } u \to \begin{cases} +\infty, \\ 0. \end{cases} \tag{37}$$

If p is to satisfy its boundary conditions it must be $O(1)$ in the limit. Then all terms in (36a) are of equal importance provided $w = O(r)$, $\Delta = O(r^{-2})$; and (36b) will only balance if $q = O(r)$. In physical terms, the recombination step is fast compared to the production step, so that there are only a few radicals present and the burning is slow. Moreover, because of the dilution of the radicals, their diffusion is weak, so that their production and recombination must be balanced locally. This description of the limit $r \to 0$ is made more precise by the estimates given above. These observations suggest that

$$p = P_0(u) + rP_1(u) + \cdots, \qquad w = rW_0(u) + r^2 W_1(u) + \cdots, \tag{38}$$

$$q = rQ_0(u) + r^2 Q_1(u) + \cdots, \qquad \Delta = r^{-2}\Delta_0 + r^{-1}\Delta_1 + \cdots \tag{39}$$

are the correct expansions; we seek to determine Δ_0 and Δ_1.

The leading terms in these expansions satisfy

$$P_0 P_0' = q_1 \Delta_0 W_0 u\, e^{-u} + q_2 \Delta_0 W_0^2,$$
$$P_0 W_0' = Q_0, \tag{40}$$
$$0 = -\Delta_0 W_0 u\, e^{-u} + \Delta_0 W_0^2,$$

from which we immediately conclude that

$$W_0 = u\, e^{-u}. \tag{41}$$

This satisfies its boundary conditions automatically; but P_0, now given by (40a), does so only if

$$\Delta_0 = 2, \tag{42}$$

and then

$$P_0 = -[1 - (1 + 2u + 2u^2)\, e^{-2u}]^{1/2}. \tag{43}$$

The remaining equation (40b) now gives

$$Q_0 = (u - 1)\, e^{-u}[1 - (1 + 2u + 2u^2)\, e^{-2u}]^{1/2}, \tag{44}$$

which also satisfies its boundary conditions automatically. In particular, the result (43) shows that $u(\eta)$ is, to first approximation, given by

$$\eta = -u + \int_u^\infty \left\{ \frac{1}{[1-(1+2u+2u^2)\, e^{-2u}]^{1/2}} - 1 \right\} du, \tag{45}$$

where an integration constant has been fixed by the boundary conditions. The corresponding $w(\eta)$ is given by the result (41). Graphs are shown in Fig. 3.

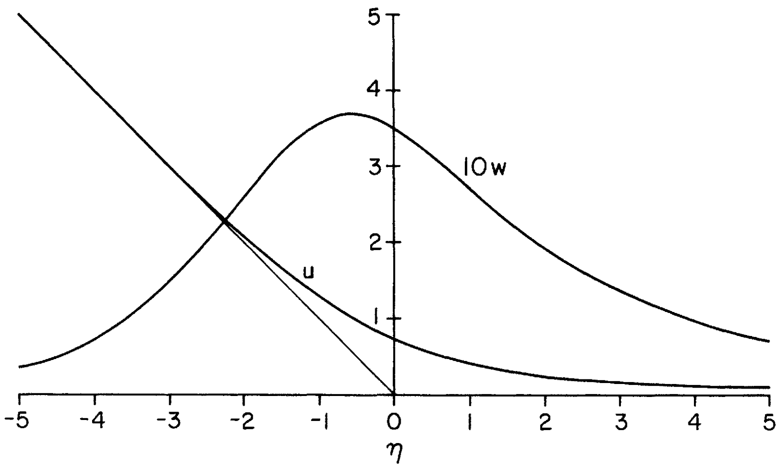

FIG. 3. *Limit profiles of u and w as $r \to 0$; valid for all q_1.*

The behavior of the approximations as η becomes large can easily be determined from these formulas; we find

$$u = \begin{cases} -\eta + O(\eta^2\, e^{2\eta}), \\ 3/(\eta-\eta_0)^2 + O(\eta-\eta_0)^{-4}, \end{cases} \quad w = \begin{cases} O(\eta\, e^{\eta}), \\ 3/(\eta-\eta_0)^2 + O(\eta-\eta_0)^{-4}, \end{cases} \quad \text{as } \eta \to \mp\infty, \tag{46}$$

which should be compared with the results (A2), (A5), and (A6) in the limit $r \to 0$; here

$$\eta_0 = \int_0^\infty \left\{ \frac{1}{[1-(1+2u+2u^2)\, e^{-2u}]^{1/2}} - 1 - \frac{\sqrt{3}}{2u^{3/2}} \right\} du = -0.8237. \tag{47}$$

The results agree for $\eta \to -\infty$ but not for $\eta \to +\infty$, since $\alpha = 3$, $\beta = 3q_2$ is not the limiting form of either possibility (i) or (ii). (Of course, no discrepancy exists because we are comparing $\lim_{\eta+\infty} \lim_{r\to 0}$ with $\lim_{r\to 0} \lim_{\eta\to+\infty}$.)

Continuing to the next terms in the expansions (38), (39) yields (after elimination of W_1)

$$(4P_0P_1 - \Delta_1 P_0^2)' = 4(1+q_2)P_0(P_0 W_0')' - 16 q_2\, e^{-u} W_0^2 \tag{48}$$

as the equation for P_1. Now

$$\int_0^\infty P_0(P_0W_0')'\,du = 2\int_0^\infty u^2(1-u)\,e^{-3u}\,du = 0,$$

$$\int_0^\infty e^{-u}W_0^2\,du = \int_0^\infty u^2\,e^{-3u}\,du = \tfrac{2}{27},$$

and $P_1(0) = P_1(\infty) = 0$. It follows, on integration from $u = 0$ to $u = \infty$, that

$$\Delta_1 = 32q_2/27. \tag{49}$$

Figure 4 shows a plot, for $q_1 = \frac{1}{2}$, of the expansion (39b) truncated at two terms. The asymptotic result provides an excellent approximation up to $r = 2$.

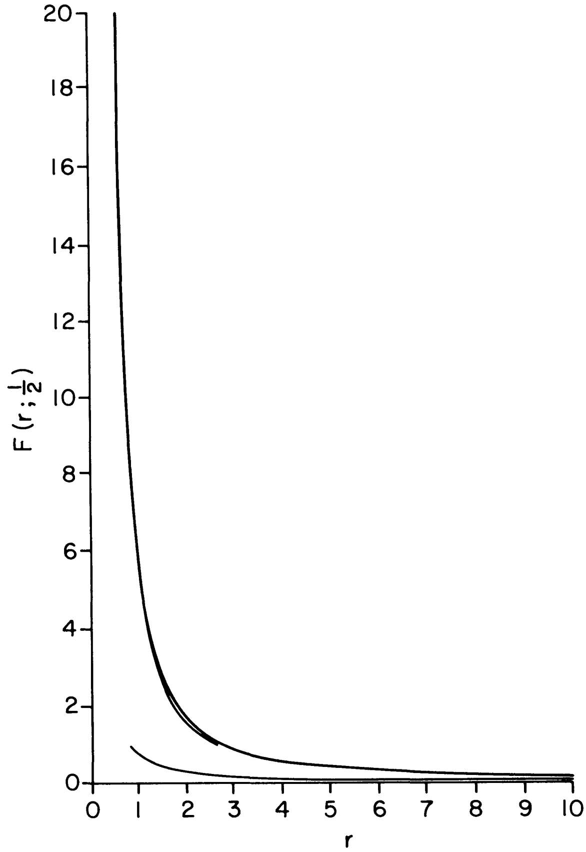

FIG. 4. *The response function $F(r;\frac{1}{2})$ with its asymptotic approximations as $r \to 0, \infty$.*

5. Behavior as $r \to \infty$. The numerical results also indicate that $\Delta \to 0$ as $r \to \infty$ on each curve $q_1 = \text{const.}$, but we now have to deal with a singular perturbation problem. To see this we note that the differential equations (26b), (27b) possess the integral

$$p + q_1 q = \text{const.} \tag{50}$$

for $\Delta = 0$, which cannot satisfy the boundary conditions (28) at both $\eta = -\infty$ and $+\infty$. (We shall find that it satisfies neither; Fig. 5 shows the adjustment that takes place for $\eta = O(\Delta^{-1/3})$.) Since the term lost in the limit is Δw^2, the difficulty is due to the slow recombination of the radicals, i.e. the smallness of D. (Note that it is more convenient to consider r as a function of Δ in this section.)

The appropriate expansions to describe the chain breaking over large distances are

$$u = \Delta^{-1/3} U_0(H) + U_1(H) + \cdots, \qquad (51)$$
$$w = \Delta^{-1/3} W_0(H) + W_1(H) + \cdots \quad \text{with } H = \Delta^{1/3}\eta;$$

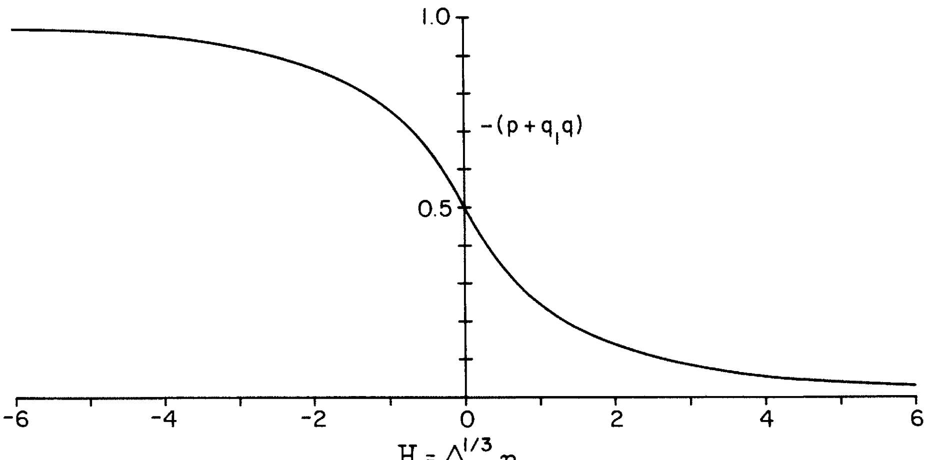

FIG. 5. *Adjustment of $p + q_1 q$ when $\eta = O(\Delta^{-1/3})$.*

then diffusion balances recombination, and the problem becomes

$$\frac{d^2 U_0}{dH^2} = q_2 \frac{d^2 W_0}{dH^2} = q_2 W_0^2 \quad \text{for } H \lessgtr 0, \qquad (52)$$

$$U_0 = \begin{cases} -H + o(1), \\ o(1), \end{cases} \qquad W_0 = o(1) \quad \text{as } H \to \mp\infty. \qquad (53)$$

We have assumed that the production of radicals is confined to $O(1)$ values of η, so that there is no exponential term in these equations. This will have to be checked a posteriori.

Equation (52a) has the solution

$$U_0 - q_2 W_0 = \begin{cases} -H, \\ 0, \end{cases} \quad \text{for } H \lessgtr 0 \qquad (54)$$

satisfying the boundary conditions. For H negative, the solution of (52b) that vanishes at infinity is

$$W_0 = 6/(H - H_0)^2 \quad \text{for } H < 0, \qquad (55)$$

where H_0 is an integration constant that must be positive if W_0 is to remain finite. Similarity of the result (A2b) should be noted. Likewise, we find

$$W_0 = 6/(H + H_0)^2 \quad \text{for } H > 0, \qquad (56)$$

where taking the integration constant to be $-H_0$ ensures that the leading term in u in the production zone is constant.

In fact, equations (52) hold to all orders, so that the later terms can be obtained by replacing H_0 with an expansion

$$H_0 \pm \Delta^{1/3} H_\mp/12 + \cdots \quad \text{for } H < 0. \tag{57}$$

Thus, we find

$$U_1 = q_2 W_1 = q_2 H_\mp/(H \mp H_0)^3 \quad \text{for } H \lessgtr 0; \tag{58}$$

matching will show that $H_- = H_+ = 0$. Here, unlike the results (46) for $r \to 0$, the behavior as η tends to both its limits can be found in the formulas (A2), (A5), (A6).

In the production zone we use the expansions

$$\begin{aligned} u &= 6q_2\Delta^{-1/3}/H_0^2 + u_1(\eta) + \Delta^{1/3} u_2(\eta) + \cdots, \\ w &= 6\Delta^{-1/3}/H_0^2 + w_1(\eta) + \Delta^{1/3} w_2(\eta) + \cdots, \end{aligned} \tag{59}$$

where the leading terms ensure matching with the expansions (51). The resulting equations for u_1 and w_1 are

$$u_1''/q_1 = -w_1'' = C(u_1 - q_2 w_1)\, e^{-u_1} \quad \text{with } C = 6r\Delta^{2/3} \exp(-6q_2\Delta^{-1/3}/H_0^2)/H_0^2. \tag{60}$$

For proper balance, C must be independent of Δ, a requirement that can only be met if (as we have assumed) the leading coefficient in u is a constant. (Taking the leading coefficient in $q_2 w$ to be anything but the same constant then leads to a structure problem that has no solution.) The question is to determine the constant C for which the system (60) has a solution satisfying appropriate boundary conditions as $\eta \to \mp\infty$, and we first eliminate w_1 from consideration.

The combination $u_1'' + q_1 w_1''$ is seen to be zero, so that

$$u_1 + q_1 w_1 = a_1 \eta + b_1, \tag{61}$$

where a_1, b_1 are integration constants. Their determination involves the next-order combination which, according to (26), (27), has the form

$$u_2 + q_1 w_2 = 18\eta^2/H_0^4 + a_2\eta + b_2, \tag{62}$$

where a_2, b_2 are integration constants and the quadratic term comes from the approximation $\Delta w^2 = \Delta(6\Delta^{-1/3}/H_0^2)^2$. A 3,2-matching of the three expansions for $u + q_1 w$ (in the production zone and on the two sides) now gives the relations

$$a_1 = -1 + 12/H_0^3 = -12/H_0^3, \quad b_1 = \mp H_\mp/H_0^3, \quad a_2 = -3H_\mp/H_0^4, \tag{63}$$

from which we conclude that

$$H_0 = 24^{1/3}, \quad H_\mp = 0, \quad a_1 = -\tfrac{1}{2}, \quad b_1 = 0. \tag{64}$$

Note that H_0 is positive, as required.

Elimination of w_1 now reduces the system (60) to the single equation

$$u_1'' = C(u_1 + q_2\eta/2)\, e^{-u_1}; \tag{65}$$

the corresponding boundary conditions (coming from matching) are

$$u_1 = \begin{cases} -(1+q_1)\eta/2 + o(1), \\ -q_2\eta/2 + o(1), \end{cases} \quad \text{as } \eta \to \mp\infty. \tag{66}$$

A problem discussed by Liñán [8], namely

$$2y'' = y \exp(\alpha x - y), \qquad y = \begin{cases} -x + (2q_1/q_2) \ln(2C/q_1^2) + o(1), \\ o(1), \end{cases} \quad \text{as } x \to \mp\infty, \tag{67}$$

then results from the transformation

(68) $$x = q_1\eta + (2q_1/q_2)\ln(2C/q_1^2), \quad y = u_1 + q_2\eta/2, \quad \alpha = q_2/2q_1$$

when q_1 is positive. (See below for $q_1 \leqq 0$.)

Liñán showed, by numerical integration, that there is a unique solution under the weaker boundary conditions

(69) $$y' \to \begin{cases} -1, \\ 0, \end{cases} \quad \text{as } x \to \mp\infty$$

when α is positive, the case of interest here ($q_2 > 0$). This result has recently been proved by Hastings and Poore [9]. From the solution, the constant

(70) $$\lim_{x\to-\infty} (y+x) \equiv \alpha^{-1}F(\alpha) = \frac{2q_1}{q_2}\ln\left(\frac{2C}{q_1^2}\right)$$

can be found as a function of α. Liñán gave the approximation

(71) $$F(\alpha) = \ln(0.6307\alpha^2 + 1.344\alpha + 1),$$

from which we deduce the formula

(72) $$C = 0.0788 + 0.1783q_1 + 0.2428q_1^2.$$

We now conclude from the definition (60c) that

(73) $$r = (H_0^2C/6)\Delta^{-2/3}\exp(6q_2\Delta^{-1/3}/H_0^2)$$

where H_0 and C are the constants (64a) and (72). Figure 4 also shows a plot, for $q_1 = \frac{1}{2}$, of this asymptotic result, which does not provide an accurate approximation (by contrast with that for $\Delta \to \infty$).

For $q_1 = 0$, we set

(74) $$u_1 = q_1 z - q_2\eta/2$$

in the problem (65), (66) and let $q_1 \to 0$, to obtain

(75) $$z'' = Cz\,e^{\eta/2}, \qquad z = \begin{cases} -\eta + o(1), \\ o(1), \end{cases} \quad \text{as } \eta \to \mp\infty.$$

The solution of the differential equation satisfying the right boundary condition is

(76) $$z = 4K_0(4C^{1/2}\exp(\eta/4)),$$

and the left boundary condition is then satisfied if

(77) $$C = 0.0788.$$

The formula (72) gives the same value for $q_1 = 0$, which is not surprising since Liñán developed his approximation (71) with a view to the limit $\alpha \to \infty$. (The above analysis is similar to his for this limit.)

For $q_1 < 0$, the boundary conditions (67b) are interchanged by the transformation (68a), i.e., they become

(78) $$y = \begin{cases} o(1), \\ -x + (2q_1/q_2)\ln(2C/q_1^2) + o(1), \end{cases} \quad \text{as } x \to \mp\infty.$$

Numerical integration of the problem (67a), (78) led to a unique solution (determining C) for

(79) $$\alpha < -1, \quad \text{i.e.,} \quad q_1 > -1, \quad q_2 < 2.$$

(The necessity of this restriction is evident from the term $\exp(\alpha x - y)$ in (67a), which otherwise does not tend to zero as $x \to +\infty$.) Figure 6 enables C to be calculated for any negative q_1 greater than -1; note that C tends to zero as $q_1 \to -1+0$ and to the value (77) as $q_1 \to 0$ from below. (The latter is to be expected, since the argument leading to this value does not depend on the sign of q_1.) The restriction (79) does not seem to be of great physical significance; it also arises as a consistency requirement, as will now be shown.

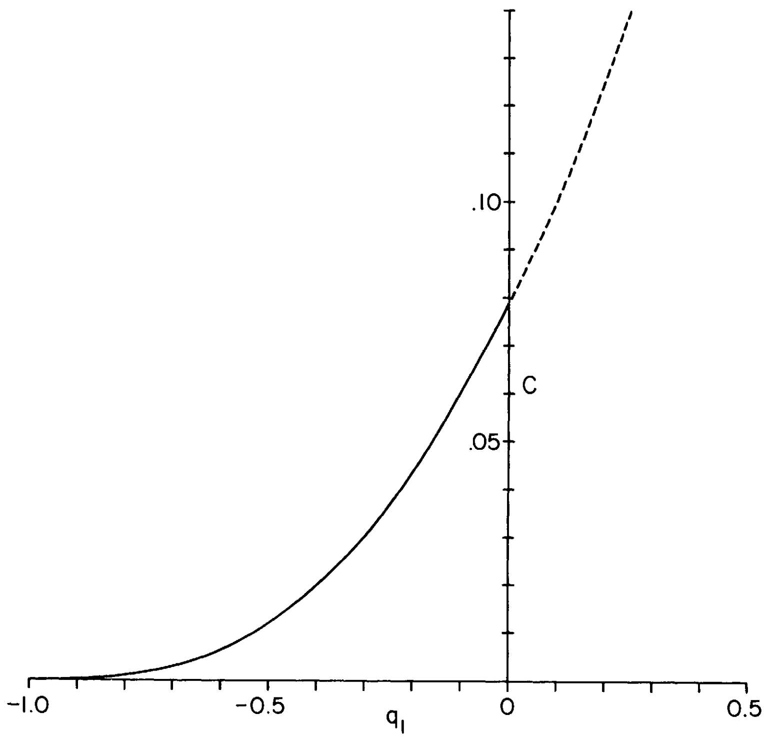

FIG. 6. *The constant* (70b) *for* $q_1 < 0$. *The dashed extension for* $q_1 > 0$ *represents the approximation* (82) *and gives a smooth transition through* $q_1 = 0$, *where the value* (77) *obtains.*

The analysis leading to (65) is based on the assumption that terms in $w(u - q_2 w)\, e^{-u}$ can be dropped for $H \leqq 0$. This will be true if either the mass fraction $u - q_2 w$ is sufficiently (i.e. exponentially) small or u is greater than its value for $H = 0$ (where the terms are not negligible). The former can be expected in $H > 0$ since $u = q_2 w$ to all algebraic orders there (cf. the remark on which the result (58) is based). The latter holds in $H < 0$ for $q_2 < 2$ (and not otherwise), since then

$$-H + 6q_2/(H - H_0)^2 > 6q_2/H_0^2 \quad \text{for all } H < 0. \tag{80}$$

The restriction (79) is now seen to be a consistency requirement also.

Appendix. Behavior near the singular points. As $\eta \to -\infty$, the system (26), (27) takes the form

$$\frac{d^2u}{d\eta^2} = q_2 \frac{d^2 w}{d\eta^2} = q_2 \Delta w^2, \tag{A1}$$

since $\exp(-u)$ may be neglected. These equations, which are independent of r, are to be solved under the appropriate boundary conditions (28). We find

$$u = -\eta + 6q_2/\Delta(\eta-\eta_-)^2, \qquad w = 6/\Delta(\eta-\eta_-)^2, \tag{A2}$$

where η_- is an integration constant; the corresponding derivatives are

$$p = -1 - 12q_2/\Delta(\eta-\eta_-)^3, \qquad q = -12/\Delta(\eta-\eta_-)^3. \tag{A3}$$

As $\eta \to +\infty$, the system (26), (27) takes the form

$$\frac{d^2u}{d\eta^2} = q_1 r\Delta w(u - q_2 w) + q_2\Delta w^2, \qquad \frac{d^2w}{d\eta^2} = -r\Delta w(u - q_2 w) + \Delta w^2, \tag{A4}$$

since $\exp(-u)$ is approximately 1. These equations, which do depend on r, are to be solved under the appropriate boundary conditions (28). By analogy with the preceding problem we seek a solution of the form

$$u = \alpha/(\eta-\eta_+)^2, \qquad w = \beta/(\eta-\eta_+)^2, \tag{A5}$$

and find the two possibilities

$$\text{(i)}\quad \alpha = 6q_2/\Delta,\ \beta = 6/\Delta, \qquad \text{(ii)}\quad \alpha = 6(1-q_1 r)/r^2\Delta,\ \beta = 6/r\Delta, \tag{A6}$$

where η_+ is an integration constant; the corresponding derivatives are

$$p = -2\alpha/(\eta-\eta_+)^3, \qquad q = -2\beta/(\eta-\eta_+)^3. \tag{A7}$$

The existence of other curves entering the singular point $\eta = +\infty$ can be inferred by writing

$$\begin{aligned} u &= \frac{\alpha}{(\eta-\eta_+)^2}\left[1 + \frac{a}{(\eta-\eta_+)^\lambda} + \cdots\right], \\ w &= \frac{\beta}{(\eta-\eta_+)^2}\left[1 + \frac{b}{(\eta-\eta_+)^\lambda} + \cdots\right] \quad \text{with } \lambda > 0 \end{aligned} \tag{A8}$$

in (A4). We find that the parameters a, b must satisfy the homogeneous linear system

$$\alpha[(\lambda+2)(\lambda+3) - q_1 r\Delta\beta]a - \Delta\beta[q_1 r(\alpha - 2q_2\beta) + 2q_2\beta]b = 0, \tag{A9}$$

$$(r\Delta\alpha\beta)a + \beta[(\lambda+2)(\lambda+3) + r\Delta(\alpha - 2q_2\beta) - 2\Delta\beta]b = 0, \tag{A10}$$

and there are four values of λ for which there is a nontrivial solution. In either of the cases (i) or (ii) we have the two values

$$\lambda = 1, -6 \quad \text{with } a = b, \tag{A11}$$

both of which may be discarded: the first corresponds to an adjustment of the existing parameter η_+, while the second is negative. In case (i) the remaining values are

$$\lambda = [-5 \pm \sqrt{1+24r}]/2 \quad \text{with } a = (2 - q_1 r)c, \quad b = q_2 rc \ (c \text{ arbitrary}), \tag{A12}$$

and there is a positive value for

$$r > 1. \tag{A13}$$

In case (ii) the remaining values are

$$\lambda = [-5 \pm \sqrt{1+24/r}]/2 \quad \text{with } a = r(2-q_1)c, \quad b = (1 - q_1 r)c \quad (c \text{ arbitrary}), \tag{A14}$$

and there is a positive value for

$$r<1. \tag{A15}$$

For $r=1$, the two cases coincide and there does not appear to be any other curve entering the singular point.

When λ is greater than 2 a better approximation than 1 must be used for $\exp(-u)$ in the original system (26), (27). Earlier terms than $(\eta-\eta_+)^{-\lambda}$ then appear in the brackets (A8). Moreover, when λ is an even positive integer $2n$, i.e. when

$$r \text{ or } 1/r=[(4n+5)^2-1]/24, \tag{A16}$$

terms $(\eta-\eta_+)^{-\lambda}$ are generated by $\exp(-u)$, so that terms $(\eta-\eta_+)^{-\lambda}\ln(\eta-\eta_+)$ are needed in the brackets (A8).

In any event, the expectation is that, for any $r\neq 1$, there is a two-parameter family of curves

$$u_-(\eta;\eta_-,\Delta),\quad w_-(\cdots),\quad p_-(\cdots),\quad q_-(\cdots) \tag{A17}$$

leaving the singular point $\eta=-\infty$, and a three-parameter family of curves

$$u_+(\eta;\eta_+,\Delta,c),\quad w_+(\cdots),\quad p_+(\cdots),\quad q_+(\cdots) \tag{A18}$$

entering the singular point $\eta=+\infty$. The first family corresponds to equations (A2), (A3), and the second to equations (A8) and derivatives, where case (i) and the formulas (A12) apply for $r>1$ while case (ii) and the formulas (A14) apply for $r<1$.

Finding the heteroclinic orbit is equivalent to solving the four equations

$$u_-(1;\eta_-,\Delta)=u_+(1;\eta_+,\Delta,c),\qquad w_-(\cdots)=w_+(\cdots), \tag{A19}$$

$$p_-(\cdots)=p_+(\cdots),\qquad q_-(\cdots)=q_+(\cdots) \tag{A20}$$

for the values of the four parameters $\eta_\pm$, Δ, c. The existence of a unique solution of this problem is currently under study.

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